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**EP 0 227 245 B1**

**Description****BACKGROUND OF THE INVENTION**5 **Field of the Invention**

The present invention relates to a recording medium suitable for recording by use of ink, such as recording by felt pens, fountain pens, pen plotters, ink jet recording devices or the like particularly, a recording medium excellent in the ink absorbency and the colorfulness, definition and gloss of recorded  
10 images, and also to an image formation process for obtaining recorded images of high image quality.

**Description of the Related Art**

Conventionally, recording media used for recording by use of ink, for example, writing by fountain pens,  
15 felt pens, ball point pens, etc. or recording by pen plotters, ink jet recording devices, etc. include ordinary paper such as high quality paper, bond paper and writing paper, or coated paper such as art paper and cast coated paper.

However, along the recent progress in recording devices such as ink jet recording devices and pen  
20 plotters, no sufficient recording performances have been achieved by the above conventional recording media.

Since a high speed recording and multi-color recording are carried out in the recent recording processes as mentioned above in such a level that can not be compared with conventional processes, the ink absorbency, the coloring performance questioned when a plural kind of ink has been deposited on the same place, the colorfulness, etc. have not reached satisfactory levels in the conventional recording media.

25 To solve these problems, there has been hitherto proposed a number of coated paper, typified by ink jet paper, having a porous ink absorbing layer on the surface of a substrate. For example, recently, Japanese Patent Laid-open Publication No. 214989/1985 discloses a sheet provided on a substrate with a porous resin ink absorbing layer. This ink absorbing layer is a porous layer having minute pores of fissures in the interior, whereby the ink absorption rate is said to be improved.

30 It is possible to improve the ink absorbency to a certain extent by providing such a porous ink absorbing layer, but, because the absorbing layer is porous, a recording medium tends to have a light diffusion property to make it impossible to obtain sharp recorded images having high optical density and glossy images also.

There is also a disadvantage that the recorded image has inferior resistance or preservability such as  
35 water resistance and abrasion resistance, because recorded images are viewed from the side of an ink recording face and thus the recording medium is constructed such that a recording agent is retained on the surface of the absorbing layer as much as possible.

European Patent Application 0049040 proposes a liquid-sorbent media constituted of a liquid-sorbent layer and a liquid-permeable layer in combination to improve surface characteristics of a substrate for pen  
40 plotters. The media are mainly characterized by their transparency, but the media are not suitable for recording apparatuses or recording methods requiring a specially rapid ink-drying property since the inherent liquid absorbency of the underlayer is retarded by the surface layer having a higher liquid absorbency, even though the media have surface characteristics improved in a certain degree.

As a means for solving such problems, there are known, for example, a recording medium disclosed in  
45 Japanese Patent Laid-open Publications No. 136480/1983 and No. 136481/1983. This recording medium comprises an ink receiving layer provided on a substrate, mainly composed of a pigment having the refractive index of 1.58 or less, and is of such a type that the recorded images are viewed from the side of the substrate. In this recording system, the performances such as water resistance at the viewing side have been well satisfied. However, although the whiteness is increased because of employment of a large  
50 amount of pigment for enhancing the whiteness of the ink receiving layer, the ink deposited tends to be adsorbed by the pigment to lessen the amount of the ink reaching the interface between the ink receiving layer and the substrate, and thus there are disadvantages such that the image density can not be made sufficiently high at the viewing side and also the colorfulness, the definition, etc. are inferior.

Recently, as the recording practiced by use of ink jet recording devices, pen plotters, etc. becomes  
55 higher in its speed and higher in its fidelity, there are increasing demands for the recording media that may have greatly improved recording performances. In other words, it has become necessary to provide recording media markedly superior to the conventional ones in all the ink absorbency, the coloring performance of a recording agent, the image quality of recorded images, the definition, the colorfulness, the

density of recorded images, the glossiness, the water resistance, the light-resistance, etc. At present, however, no recording media have been obtained that can satisfy all of these recording performances simultaneously.

## 5 SUMMARY OF THE INVENTION

In one aspect the invention provides a recording medium for use with aqueous ink, said medium comprising an ink transporting layer and an ink retaining layer, the ink retaining layer having a greater absorption capacity than the ink transporting layer, the ink transporting layer being effective to receive and  
10 pass through the ink and having a high affinity for the liquid medium in the ink and a low affinity for colouring material in the ink wherein the ink transporting layer is light diffusive and wherein the ink retaining layer is light transmissive.

In a further aspect the invention provides a process for forming an image, comprising applying droplets of a recording liquid containing a dye, water and a water soluble organic solvent onto a recording medium  
15 as aforesaid to form an image. The above recording medium can exhibit good glossiness on its surface and can produce recorded images having excellent image density, the recording medium may exhibit excellent water resistance, abrasion resistance, durability and visual qualities.

In one form of the invention the medium may comprise a heat and/or pressure adherent ink transporting layer, and after the ink droplets have been applied to the ink transporting layer the ink transporting layer  
20 may be attached to a substrate. In that case the invention enables images to be produced on the surfaces of such substrate as ordinary paper, metal, glass, plastic or the like without any special treatment of the surface of that substrate.

## DETAILED DESCRIPTION OF THE PREFERRED EMBODIMENTS

25 The recording medium of the present invention, in which the recording is basically practiced by introducing ink into the ink transporting layer, is principally characterized by very high image density of images viewed from the ink retaining layer side (or the substrate side) as compared with the image density of images viewed from the ink transporting layer side.

30 More specifically, the ink transporting layer constituting a recording medium of the present invention is liquid-permeable, and has a function to immediately absorb and permeate a recording liquid attached on its surface, and on the other hand, the ink retaining layer has a function to absorb and retain the recording liquid or a recording agent migrating from said ink transporting layer.

In this case, the ink transporting layer must have high affinity to a liquid medium in the recording liquid,  
35 and at the same time must have low affinity, on the contrary, to the recording agent (i.e., a colorant such as dye and pigment, and a material having a coloring property). Accordingly, the ink transporting layer must be constituted by selecting the materials that have properties such as wettability, permeability and diffusibility with respect to the ink, and have not properties such as absorbency, permeability and reactivity with respect to the recording agent.

40 The ink transporting layer not having the properties of wettability, permeability and diffusibility and the like to the recording medium may result in no immediate permeation of a recording liquid into the interior of the ink transporting layer when the recording liquid is applied to the ink transporting layer, thereby lowering the recording liquid absorbency. Further, the recording liquid tends to remain in such an transporting layer without reaching rapidly the ink retaining layer to make it impossible to obtain recorded images having good  
45 water resistance.

The ink transporting layer having properties of absorbency, permeability and reactivity and the like to the recording agent may result in that a recording agent remains on the surface or in the inside of the ink transporting layer without reaching the ink retaining layer, to make it impossible to obtain sufficiently colorful recorded images having high optical density.

50 On the other hand, the ink retaining layer, which absorbs and captures a recording liquid temporarily absorbed in the ink transporting layer, must have stronger absorption capacity to the recording liquid than the ink transporting layer has. Therefore, the ink retaining layer must have high affinity not only to the recording liquid medium, but also to the recording agent.

The present invention will be described below in detail based on working examples.

55 The recording medium of the present invention is constituted of a substrate as a support, an ink retaining layer formed on said support to substantially absorb and capture a recording liquid or a recording agent, and an ink transporting layer formed on the ink retaining layer and having liquid-permeability to directly accept the recording liquid but not substantially allow it to remain.

The substrate may not necessarily be required if the ink transporting layer or the ink retaining layer may function simultaneously as a substrate.

The substrate used in the present invention may include those conventionally known, for example, plastic films or plates made of polyethylene terephthalate, polycarbonate resins, polystyrene resins, polysulfone resins, polybutylene terephthalate resins, polypropylene resins, methacrylic resins, diallyl phthalate resins, unsaturated polyester resins, cellophane, acetate plastics, cellulose diacetate, cellulose triacetate, celluloid, vinyl chloride resins etc., or glass plates.

In the recording medium of the present invention when observed from the side opposite to the recording face, the substrate is required to be transparent.

In such an occasion, the substrate may be applied with any processing if it can finally retain the transparency. For instance, it is possible to apply on it desired patterns or gloss (appropriate gloss or silky pattern).

It is also possible to impart water resistance, abrasion resistance and blocking resistance to the image-viewing face of the recording medium by selecting materials having water resistance, abrasion resistance and blocking resistance as the substrate.

The substrate may have a thickness ranging between 1 and 5000  $\mu\text{m}$ , preferably between 3 and 1000  $\mu\text{m}$ , more preferably between 5 and 500  $\mu\text{m}$ .

In order to improve adhesion between the ink retaining layer and the substrate, the substrate may be pre-treated by corona treatment, alkali agent coating, etc.

The ink transporting layer constituting the recording medium of the present invention is required to have liquid-permeability and light diffusing property.

The liquid-permeability mentioned in the present invention refers to the property that may immediately permeate a recording liquid and may not substantially allow a recording agent in the recording liquid to remain in the ink transporting layer.

In the present invention, as a preferred embodiment for improving the liquid-permeability, the surface or the inside of the ink transporting layer may have porous structure containing fissures or communicated holes (including those of micro size). For example, in the recording with an aqueous ink, the following embodiments can be enumerated:

- (1) an embodiment wherein the layer is constituted of non-dyeable particles and a binder, and has fissures internally;
- (2) an embodiment wherein other materials are dispersed in a coating, and the inside of the layer is made porous by treating it with a solvent;
- (3) an embodiment wherein a resin is dissolved in a mixed solvent so that a high boiling solvent may act as a poor solvent for the resin to make porous the inside of the layer; and
- (4) an embodiment wherein a foamable material is contained when coating so that the inside of the layer may be made porous.

Materials used here should be selected from those non-swelling to water and a solvent in ink, and not dyeable to a dye in ink.

A preferred embodiment of the ink transporting layer according to the present invention, satisfying the above properties is, for example, the embodiment wherein the layer is constituted of non-dyeable particles and a binding agent.

As the non-dyeable particles satisfying the above properties, there may be used at least one of organic resin particles made of thermoplastic resins or thermosetting resins including, for example, organic resin powder, an emulsion and a suspension of polyethylene resins, methacrylic resins, elastomers, polystyrene resins, ethylene-vinyl acetate copolymer, styrene-acrylic copolymer, fluoroplastics, polyamide resins, polypropylene resins, methacrylic resins, guanamine resins, melamine formaldehyde resins, urea formaldehyde resins, silicones, celluloses, benzoguanamine resins, SBR (styrene-butadiene rubber), polyesters, thermoplastic elastomers, etc.; particles of inorganic pigment treated so as to be made non-porous; or the like.

The binder used in the present invention has a function to bind the above particles each other and/or the ink retaining layer, and is required to be non-dyeable to the recording agent as in the case of the above particles.

As preferable materials for the binder, there may be used any of known materials of those having the above function, for example, one or more resins of ionomer resins, acrylonitrile-styrene copolymer, ethylene-vinyl acetate copolymer, vinylidene chloride resins, polyvinyl acetate resins, styrene-acrylic copolymer, phenolic resins, isobutylene-maleic anhydride copolymer, epoxy resins, polyvinylidene chloride resins, xylene-formaldehyde resins, cumarone resins, ketone resins, polyvinyl alcohol, polyvinyl butyral resins, polyvinyl pyrrolidone, acrylic resins, starch, carboxymethyl cellulose, methyl cellulose, ethyl cellulose, styrene butadiene rubber, gelatin, casein, polyurethane resins, polychloroprene resins, melamine

formaldehyde resins, nitrile rubber, urea formaldehyde resins, etc.

To the ink transporting layer, it is also allowable to add particles having higher refractive index, for example, pigment particles, in such amount that may not impair its ink permeability.

If necessary, various additives, for example, a surfactant, a penetrating agent, etc. may be added to the ink transporting layer in order to improve the above functions as an ink transporting layer.

The mixing ratio (by weight) of the non-dyeable particles and the binder in the ink transporting layer (particles/binder) may range between 1/3 and 70/1, preferably between 1/1 and 50/1, more preferably between 3/1 to 20/1. The mixing ratio of less than 1/3 may result in too small fissures and communicated holes in the ink transporting layer and decrease in the absorbability of the recording liquid. The mixing ratio of more than 70/1, on the other hand, may result in insufficient adhesion between the particles themselves or the ink retaining layer and the particles, whereby the ink transporting layer can not be formed.

The ink transporting layer may have a thickness, though depending on the amount of the recording liquid, of 1 to 300  $\mu\text{m}$ , preferably 5 to 200  $\mu\text{m}$ , more preferably 10 to 150  $\mu\text{m}$ .

Referring to the porous ink retaining layer which substantially captures the recording liquid or the recording agent, it absorbs and capture the recording agent passed through the ink transporting layer to retain it substantially permanently. Therefore, it is required for the ink retaining layer to have stronger absorption capacity than the ink transporting layer.

This is because, if the absorption power of the ink retaining layer is less than that of the ink transporting layer, it follows that the recording liquid applied on the surface of the ink transporting layer remains retained in the ink transporting layer when a top portion of the recording liquid reached the ink retaining layer after passing through the ink transporting layer, whereupon the recording liquid permeates and diffuse at the interface between the ink transporting layer and the ink retaining layer in the lateral direction in the ink transporting layer. As a result, the definition of recorded images will be lowered to make it impossible to form images of high quality.

The ink retaining layer, as mentioned before, is required to be transparent when recorded images are viewed from the side opposite to the recording face.

The ink retaining layer satisfying the above requirements is preferably constituted of a light-transmissive resin capable of absorbing the recording agent and/or a light-transmissive resin having solubility and swelling property to the recording liquid.

For example, when an aqueous recording liquid containing as the recording agent an acidic dye or a direct dye, the ink retaining layer is constituted of a cation resin having absorbency to the dye and/or a hydrophilic polymer having swelling property to the aqueous recording liquid.

The above polymer may include, for example, the following:

(1) block copolymers or graft copolymers having hydrophilic segments and hydrophobic segments within the molecule:

Such block copolymers or graft copolymers are water-insoluble as a whole, but hydrophilic. The hydrophilic segments of such polymers are, for example, segments formed by polymerization of two or more vinyl monomers having hydrophilic groups such as a carboxyl group, a sulfonic acid group, a hydroxyl group, an ether group, an acid amide group, methylol groups of these, a primary to tertiary amino group and a quaternary ammonium group. Examples of such hydrophilic monomer may include acrylic or methacrylic acid, maleic anhydride, vinyl sulfonic acid, sulfonated styrene, vinyl acetate, monoacrylates or monomethacrylates or monomaleates of polyols such as ethylene glycol, acrylic or methacrylic amides or methylols of these, mono- or dialkylaminoethyl acrylate or methacrylate, quaternary compounds of these, vinyl pyrrolidone, vinyl pyrimidine, etc.

The hydrophobic polymer segments are polymers of two or more of monomers including olefins such as ethylene, propylene and butylene; aromatic vinyl compounds such as styrene, methylstyrene and vinyl naphthalene; halogenated olefins such as vinyl chloride, vinylidene chloride and vinylidene fluoride; various alcohol esters of unsaturated carboxylic acids such as acrylic or methacrylic acid and crotonic acid; etc.

It is also possible as a matter of course to use water-soluble polymers other than the above as the hydrophilic polymer segments or the hydrophobic polymer segments, including, for example, natural or synthetic hydrophilic polymers such as albumin, gelatine, casein, starch, cation starch; natural resins such as gum arabic and sodium alginate, polyvinyl alcohol, polyamide, polyacrylamide, polyvinyl pyrrolidone, polyethylene imine, polyvinyl pyridylum halide, melamine resin, polyurethane, polyester and sodium polyacrylate; or natural or synthetic hydrophobic polymers modified by making these polymers insoluble in water.

## (2) Crosslinked water-soluble polymers:

These are obtained by crosslinking the water-soluble polymers mentioned above or those mentioned below with use of suitable crosslinking agents or radiations to the degree that may be made insoluble in water without losing the hydrophilic nature.

## (3) Polymer complex:

Polymer complex is comprised of two or more of water-soluble or hydrophilic polymers which are different from each other and may act on each other. There is produced a mixture having different nature from either of the original polymers. For example, two or more of polymers are strongly bonded through electrostatic force between ions, hydrogen bonding, van der Waals force, partial migration of electrical charge, etc.

There may be used various ones as the polymer complex, but most preferable in the present invention is a polymer complex comprising a basic polymer and an acidic polymer.

The materials constituting the ink retaining layer may not be particularly limited if they have a function to absorb and capture the recording liquid and is capable of forming a non-porous layer.

The ink retaining layer may have a thickness sufficient for absorbing and capturing the recording liquid, which may range, though variable depending on the amount of the recording liquid, between 1 and 70  $\mu\text{m}$ , preferably between 2 and 50  $\mu\text{m}$ , and more preferably between 3 and 30  $\mu\text{m}$ .

The method of forming the ink retaining layer and the ink transporting layer on the substrate may preferably comprise preparing a coating liquid by dissolving or dispersing the material in a suitable solvent mentioned above, applying the coating liquid on the substrate by a conventionally known method such as roll coating, rod bar coating, spray coating and air knife coating, followed immediately by drying. Alternatively, there may be used the hot melt coating mentioned before or a method comprising once making a single sheet from the above-mentioned materials, and then laminating the sheet on the substrate.

When the ink retaining layer is provided on the substrate, however, strong adhesion is required between the substrate and the ink retaining layer so that no space or gap may be present therebetween. The presence of the space or gap between the substrate and the ink retaining layer may result in irregular reflection of recorded images at the surface to lower substantial optical density of images undesirably.

Means for forming images by using the recording medium of the present invention may include recording tools and recording devices using a recording liquid containing a recording agent, such as fountain pens, ball point pens, felt pens, pen plotters, ink mist, ink jet and a variety of printing.

Of these recording tools and recording devices, the ink jet recording device and the pen plotters are preferable from a viewpoint of the high speed image recording.

The recording liquid for making recording on the recording medium of the present invention may preferably include conventionally known aqueous and/or oily recording-liquids, and is required to have a viscosity of 1 Pa.s (1000 cps) or less, preferably 100 mPa.s (1000 cps) or less, and more preferably 50 mPa.s (50 cps) or less, in order to immediately permeate into the ink transporting layer and to be absorbed and captured in the ink retaining layer.

Considering the stability to fire or the environmental pollution, the water recording-liquid is preferred. As the recording agent contained in the recording liquid, there may be used any of conventionally known colorants such as dyes and pigments, and/or those having coloring property.

For example, the recording agent used for the ink jet recording may preferably include water-soluble dyes typified by direct dyes, acidic dyes, basic dyes, reactive dyes, food dyes, edible dyestuff, etc., and, as those capable of giving images achieving satisfactory fixing performance, coloring performance, sharpness, stability, light resistance and other required performances when used in combination with the recording medium, preferably include, for example, direct dyes such as C.I. Direct Black 17, 19, 32, 51, 71, 108 and 146; C.I. Direct Blue 6, 22, 25, 71, 86, 90, 106 and 199; C.I. Direct Red 1, 4, 17, 28 and 83; C.I. Direct Yellow 12, 24, 26, 86, 98 and 142; C.I. Direct Orange 34, 39, 44, 46 and 60; C.I. Direct Violet 47 and 48; C.I. Direct Brown 109 and C.I. Direct Green 59, and acid dyes such as C.I. Acid Black 2, 7, 24, 26, 31, 52, 63, 112 and 118; C.I. Acid Blue 9, 22, 40, 59, 93, 102, 104, 113, 117, 120, 167, 229 and 234; C.I. Acid Red 1, 6, 32, 37, 51, 52, 80, 85, 87, 92, 94, 115, 180, 256, 317 and 315; C.I. Acid Yellow 11, 17, 23, 25, 29, 42, 61 and 71; C.I. Acid Orange 7 and 19 and C.I. Acid Violet 49. Besides these, C.I. Basic Black 2; C.I. Basic Blue 1, 3, 5, 7, 9, 24, 25, 26, 28 and 29; C.I. Basic Red 1, 2, 9, 12, 13, 14 and 37; C.I. Basic Violet 7, 14 and 27; C.I. Food Black 1 and 2; etc. may be also used.

The above dyes are examples particularly preferable for the ink applicable to the recording process of the present invention, and dyes for the ink used in the present invention may not be limited to these.

These water-soluble dyes are generally used in conventional ink in an amount of such a proportion that may hold about 0.1 to 20 % by weight, and may be used in the similar proportion also in the present invention.

The solvent preferably used in the ink used in the present invention includes water or a mixed solvent comprising water and a water-soluble organic solvent. Particularly preferable solvent is a mixed solvent comprising water and a water-soluble solvent, and the water-soluble organic solvent includes one containing a polyhydric alcohol having an effect to prevent ink from drying. As the water, preferably used is not ordinary water containing various ions, but deionized water. The water-soluble organic solvent used by mixing with water may include, for example, alkyl alcohols having 1 to 4 carbon atoms, such as methyl alcohol, ethyl alcohol, n-propyl alcohol, isopropyl alcohol, n-butyl alcohol, sec-butyl alcohol, tert-butyl alcohol and isobutyl alcohol; amides such as dimethylformamide and dimethylacetamide; ketones or ketone alcohols such as acetone and diacetone alcohol; ethers such as tetrahydrofuran and dioxane; polyalkylene glycols such as polyethylene glycol and polypropylene glycol; alkylene glycols containing alkylene groups having 2 to 6 carbon atoms, such as ethylene glycol, propylene glycol, butylene glycol, triethylene glycol, 1,2,6-hexanetriol, thiodiglycol, hexylene glycol and diethylene glycol; glycerin; lower alkyl ethers of polyhydric alcohols such as ethylene glycol methyl (or ethyl) ether, diethylene glycol methyl (or ethyl) ether and triethylene glycol monomethyl (or monoethyl); N-methyl-2-pyrrolidone, 1,3-dimethyl-2-imidazolidinone, etc. Of these numerous water-soluble organic solvents, preferably used are polyhydric alcohols such as diethylene glycol and lower alkyl ethers of polyhydric alcohols such as triethylene glycol monomethyl (or monoethyl) ether.

The above water-soluble organic solvent may be contained in the ink in an amount ranging between 0 and 95 % by weight, preferably between 10 and 80 % by weight, and more preferably between 20 and 50 % by weight.

Besides the foregoing components, if necessary, the ink used in the present invention may contain a surfactant, a viscosity modifier, a surface tension regulator, etc.

The image formation process of the present invention will be described below.

In the present invention, images are recorded by applying the recording liquid to the ink transporting layer of the recording medium.

After recording, it is possible to make transparent the ink transporting layer to view the images from the side at which the ink was applied, but, in order to make the most of the characteristic feature of the present invention, i.e., the higher density of the images viewed from the ink retaining layer side (or the substrate side) as compared with the density of the images viewed from the ink transporting layer side, it is preferable to apply recording droplets based on mirror images of the recording images to the ink transporting layer of the recording medium, and view the images from the ink retaining layer side.

In the present invention, the image density (A) measured from the substrate side (or the ink retaining layer side) reaches about 1.2 times or more of the image density (B) measured from the ink transporting layer side, and can be also very readily made 1.5 times or more or 2.0 times or more.

Another image formation process using the recording medium of the present invention comprises recording images by applying recording droplets to the ink transporting layer, adhering the transporting layer of the recording medium on which images have been recorded, to the substrate made of metal, plastic, cloth, paper, etc., followed by application of heat to, or contact bonding of, both of these, to form recorded images on the substrate by using ink.

In this instance, materials for the ink transporting layer must be selected so that the fusing temperature for the ink transporting layer may be in the range of 70 to 150 °C in practical use.

Although no images could not have been formed on metal or plastic by the conventional recording processes, the process of the present invention has made it possible to readily form images of high quality and high density by using ink, on such a substrate that could not have been recorded unless a special treatment is applied on its surface.

The recording medium of the present invention, constructed as mentioned above, has superior effects that could not have been achieved conventionally, when the recorded images are viewed from the side opposite to the recording face, i.e., the ink-retaining-layer side or the substrate side, although it is not impossible to view the recorded images from the side on which images are recorded by using a recording liquid as in ordinary paper. More specifically, the diffusible reflection is minimized on the image viewing side because of the light-transmissive ink retaining layer, thereby obtaining high optical density of images that cannot be achieved when images are recorded on a porous sheet such as paper by use of a recording liquid.

It is also possible to provide sharp recorded images because the absorbency of a recording liquid and the definition of recorded images have been improved by the liquid-permeability imparted to the ink

transporting layer acting as a recording face and the fissures or communicated holes formed internally.

Further, when a transparent substrate is used as a support, in addition to the effects owing to the light-transmissive substrate, the recorded images are endowed with glossiness, water-resistance, weathering resistance and abrasion resistance.

Still further, since the colorant which forms images, a dye for example, is not retained on the surface of the recording medium but is mostly present in the ink retaining layer interposed between the substrate and the ink transporting layer, the images are less influenced externally. Accordingly, the migration of dyes due to moisture absorption or the color change or degradation thereof by light have been remarkably ameliorated.

The recording medium of the present invention is markedly superior in the optical density of recorded images and the operational facility during the image formation processing, as compared with the conventional method in which a transparent film is laminated on the surface of recorded images.

As described above, the present invention has good effects in the absorbency of recording liquid, the optical density of recorded images, the definition, the glossiness, the water resistance, the light resistance, the abrasion resistance and the operational facility during the image formation processing.

It has been also made possible according to the process of the present invention to readily form recorded images having the above respective performances on glass, plastic, cloth and the like.

The present invention will be specifically described below based on Examples. In Examples, the quantity "parts" is based on weight.

#### Example 1

A polyethylene terephthalate film (100  $\mu\text{m}$  thick; produced by Toray Industries, Inc.) used as a light-transmissive substrate was coated on its surface with the following Composition A by means of a bar coater so as to have a dried film thickness of 8  $\mu\text{m}$ , followed by drying in a drying stove at 120 °C for 5 minutes.

Composition A:	
Polyvinyl pyrrolidone PVP K-90; produced by GAF; 10 % DMF solution)	88 parts
Novolac phenol resin (Resitop PSK-2320; produced by Gun-ei Chemical Industry Co., Ltd.; 10 % DMF solution)	12 parts

Subsequently, the above coating was further coated with the following Composition B by means of a bar coater so as to have a dried film thickness of 30  $\mu\text{m}$ , followed by drying in a drying stove at 80 °C for 10 minutes.

Composition B:	
Low density polyethylene resin (Chemiparl M-200; produced by Mitsui Petrochemical Industries, Ltd; solid content; 40 %; particle size: 5 $\mu\text{m}$ )	100 parts
Ethylene/vinyl acetate copolymer resin (Chemiparl V-100; produced by Mitsui Petrochemical Industries, Ltd; solid content: 40 %; particle size 5 $\mu\text{m}$ )	10 parts
Polyoxyethylene octyl phenyl ether(Emulgen 810; produced by Kao Corporation)	0.2 part

The recording medium thus obtained was white and opaque. On this recording medium, ink jet recording was carried out with use of four kinds of ink shown below and with use of a recording device (orifice size: 18 x 25 microns; driving voltage: 22.5 V; frequency: 2 kHz) equipped with an on-demand type ink jet recording head, in which bubbles were generated by means of a heating resistor and a recording liquid was ejected under the pressure thereof. The makeup of the four kinds of the recording liquids employed are shown in Table 1. Recorded matters thus obtained were tested according to the following procedures to evaluate whether they can sufficiently answer the object of the present invention.

(1) Ink absorbency was evaluated by measuring the time for the recorded matters, having been left at room temperature after the ink jet recording, to be sufficiently dried and fixed without staining fingers with ink even when a recorded portion was touched.



(2) Optical density of images (O.D.) was measured from the side (B) on which ink was applied and its reverse side (A), on black ink recorded portions and by using Macbeth densitometer TR-524.

(3) Image surface gloss was evaluated by measuring 45° specular gloss of the surface of images to be viewed according to JIS Z8741.

(4) Operational facility was evaluated by designating as "o" where no cumbersome handling was required during the image formation processing, and as "X" where cumbersome handling was required.

(5) Water resistance of images was evaluated by measuring the image densities of solid black color printed images (from the ink retaining layer side) before and after having been immersed in flowing water for 5 minutes, with use of Macbeth densitometer TR-524, and is represented by percentage obtained by dividing the density after immersion by the density before immersion. The higher the value, the better is the water resistance.

Overall evaluations were made based on the results thus obtained. Results are shown in Table 2.

The overall evaluations were made by designating as "o" where the recording liquid was immediately absorbed, the suitability to ink jet recording was excellent, and the glossiness of image viewing surface, the sharpness of recorded images, the operational facility during image formation processing and the water resistance of images were good, and as "X" where any one of the ink jet suitability, the glossiness of image viewing surface, the operational facility during image formation processing and the water resistance of images was insufficient.

Table 1

Yellow ink (makeup):	
C.I. Direct Yellow 86	2 parts
N-methyl-2-pyrrolidone	10 parts
Diethylene glycol	20 parts
Polyethylene glycol #200	15 parts
Water	55 parts
Magenta ink (makeup):	
C.I. Acid Red 35	2 parts
N-methyl-2-pyrrolidone	10 parts
Diethylene glycol	20 parts
Polyethylene glycol #200	15 parts
Water	55 parts
Cyan ink (makeup):	
C.I. Direct Blue 86	2 parts
N-methyl-2-pyrrolidone	10 parts
Diethylene glycol	20 parts
Polyethylene glycol #200	15 parts
Water	55 parts
Black ink (makeup):	
C.I. Food Black 2	2 parts
N-methyl-2-pyrrolidone	10 parts
Diethylene glycol	20 parts
Polyethylene glycol #200	15 parts
Water	55 parts

#### Example 2

A polyethylene terephthalate film used in Example 1 as a light-transmissive substrate was coated on its surface with the following Composition C by means of a bar coater so as to have a dried film thickness of 5  $\mu\text{m}$ , followed by drying in a drying stove at 110° C for 10 minutes.

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Composition C:	
Polyvinyl pyrrolidone PVP K-90; produced by GAF; 10 % DMF solution)	84 parts
Styrene/acrylic acid copolymer (Oxylac SH-2100; produced by Nippon Shokubai Kagaku Kogyo Co., Ltd.; 10 % DMF solution)	16 parts

Subsequently, the above coating was further coated with the following Composition D by means of a bar coater so as to have a dried film thickness of 40  $\mu\text{m}$ , followed by drying in a drying stove at 120 °C for 10 minutes.

Composition D:	
Polymethacrylate resin (Microsphere M-100; produced by Matsumoto Yushi-Seiyaku Co., Ltd.; mean particle size: 5 $\mu\text{m}$ )	100 parts
Ionomer resin (Chemipearl SA-100; produced by Mitsui Petrochemical Industries, Ltd; solid content: 35 %)	30 parts
Sodium dioctylsulfosuccinate (Pelex OT-P; produced by Kao Corporation; solid content: 70 %)	0.15 part
Water	40 parts

The recording medium thus obtained was white and opaque. On this recording medium, ink jet recording was carried out in the same manner as in Example 1.

Evaluations of the recording medium were also made following the procedures in Example 1. Results are shown in Table 2.

## Example 3

A polyethylene terephthalate film used in Example 1 as a light-transmissive substrate was coated on its surface with the following Composition E by means of a bar coater so as to have a dried film thickness of 10  $\mu\text{m}$ , followed by drying in a drying stove at 100 °C for 12 minutes.

Composition E:	
Comb polymer* (25 % Methyl Cellosolve solution)	60 parts
Monoalkyl Esters of Poly(methyl vinyl ether/maleic acid) (Gantrez ES-425; produced by GAF; 10 % solution in water/ethanol)	40 parts

\* A graft polymer of 80 parts of backbone chain (copolymer of 64 parts of 2-hydroxyethyl methacrylate and 16 parts of dimethyl acrylamide grafted with 20 parts of MMA macromer)

Subsequently, the above coating was further coated with the following Composition F by means of a bar coater so as to have a dried film thickness of 30  $\mu\text{m}$ , followed by drying in a drying stove at 70 °C for 10 minutes.

Composition F:	
Thermoplastic elastomer resin (Chemipearl A-100; produced by Mitsui Petrochemical Industries, Ltd.; solid content: 40 %; particle size: 5 $\mu\text{m}$ )	100 parts
Ionomer resin (Chemipearl SA-100; produced by Mitsui Petrochemical Industries, Ltd; solid content: 35 %)	10 parts
Polyoxyethylene (Emulgen A-500; produced by Kao Corporation)	0.2 part

Example 4

Composition E and Composition F used in Example 3 were coated on a polytetrafluoroethylene film in the same manner as in Example 3, and thereafter the polytetrafluoroethylene film was peeled off to obtain a white opaque recording medium. On the recording medium, ink jet recording was applied in the same manner as in Example 1.

Evaluations of the recording medium were also made following the procedure in Example 1.

Results of the above are shown in Table 2.

10 Comparative Example 1

Using commercially available ink jet paper (IJ mat-coat paper NM; produced by Mitsubishi Paper Mills, Ltd.) as a recording medium, ink jet recording was carried out in the same manner as in Example 1. Evaluations of the recording medium were also made following the procedures in Example 1. Results are shown in Table 2.

Comparative Example 2

Using ink jet paper used in Comparative Example 1 as a recording medium, ink jet recording was carried out in the same manner as in Example 1. Thereafter, using a laminator (MS Lamipet L-230; produced by Meiko Shokai Co., Ltd.), a laminating film (MS pouch film; 100  $\mu$ m thick; produced by Meiko Shokai Co., Ltd.) was laminated on the image recording face. Evaluations of the resultant medium were made following the procedures in Example 1. Results are shown in Table 2.

25 Comparative Example 3

Using commercially available glossy paper (SA Kinfuji Super Art; produced by Kanzaki Paper MFG. Co., Ltd.) as a recording medium, ink jet recording was carried out in the same manner as in Example 1. Evaluations of the recording medium were also made following the procedures in Example 1. Results are shown in Table 2.

Comparative Example 4

Using a polyethylene terephthalate film (100  $\mu$ m thick; produced by Toray Industries, Inc.) as a light-transmissive substrate, the substrate was coated with the following composition G by means of a bar coater so as to have a dry spread of 15 g/m<sup>2</sup>, followed by drying in a drying stove at 100 °C for 5 minutes.

## Composition G:

Colloidal silica (Snowtex 20L; produced by Nissan Chemical Industries, Ltd.; solid content: 20 %)	100 parts
Polyvinyl alcohol (PVA-117; produced by Kuraray Co., Ltd.; 10 % aqueous solution)	30 parts

On the comparative recording medium thus obtained, recording was carried out in the same manner as in Example 1 to make evaluations of the recording medium. Results are shown in Table 2.

In Comparative Examples 1 to 3, the image surface gloss (%) and the water resistance (%) was determined by measuring the gloss and the density at the surface on which ink was applied.

Table 2

	Ink absorbency	Optical density of images (A)	Optical density of images (B)	Image surface gloss (%)	Water resistance (%)	Operational facility	Overall evaluation
Example 1	1 sec.	2.08	0.57	116.0	105	o	o
Example 2	1 sec.	1.90	0.45	121.0	102	o	o
Example 3	1 sec.	2.20	0.60	118.0	115	o	o
Example 4	1 sec.	1.90	0.50	95.0	110	o	o
Comparative Example 1	1 sec.	0.13	1.55	4.3	112	o	x
Comparative Example 2	1 sec.	0.20	1.75	118.0	100	x	x
Comparative Example 3	10 min.	0.15	1.42	30.1	28	o	x
Comparative Example 4	1 sec.	1.72	1.68	110.0	8	o	x

## 55 Example 5

A polyethylene terephthalate film (100  $\mu$ m thick; produced by Toray Industries, Inc.) used as a light-transmissive substrate was coated on its surface with the following Composition H by means of a bar coater

so as to have a dried film thickness of 6  $\mu\text{m}$ , followed by drying in a drying stove at 110 °C for 5 minutes.

Composition H:	
Comb polymer* (25 % Methyl cellosolve solution)	55 parts
Monoalkyl esters of poly(methyl vinyl ether/maleic acid) (Gantrez ES-425; produced by GAF; 10 % solution of water/ethanol)	45 parts

\* A graft polymer of 80 parts of backbone chain (copolymer of 64 parts of 2-hydroxyethyl methacrylate and 16 parts of dimethyl acrylamide grafted with 20 parts of MMA macromer)

Subsequently, the above coating was further coated with the following Composition I by means of a bar coater so as to have a dried film thickness of 25  $\mu\text{m}$ , followed by drying in a drying stove at 75 °C for 10 minutes.

Composition I:	
Low density polyethylene resin (Chemipearl M-200; produced by Mitsui Petrochemical Industries, Ltd; solid content: 40 %)	100 parts
Ionomer resin (Chemipearl SA-100; produced by Mitsui Petrochemical Industries, Ltd; solid content: 35 %)	11 parts
Sodium dioctylsulfosuccinate (Pelex OT-P; produced by Kao Corporation; solid content: 70 %)	0.2 part

The recoding medium thus obtained was white and opaque. On this recording medium, ink jet recording was carried out in the same manner as in Example 1.

In respect of the recorded matters thus obtained, a polyethylene terephthalate film (100  $\mu\text{m}$  thick; produced by Toray Industries, Ltd.) was laminated on the ink transporting layer, and then fused by using a laminator (MS Lamipet L-230; produced by Meiko Shokai Co., Ltd.).

Recorded matters thus obtained were tested in the same manner as in Example 1 to see whether they can sufficiently answer the object of the present invention, by evaluating the ink absorbency, the optical density (A) of images and the image surface gloss. The adhesion between the substrate and the recording medium was also evaluated, and designated as "o" where the adhesion was good and as "X" where they were not adhered or readily peeled off.

Overall evaluations were made based on the results thus obtained. Results are shown in Table 2.

The overall evaluations were made by designating as "o" where the recording liquid was immediately absorbed, the suitability to ink jet recording was excellent, the image viewing surface had glossiness, the image viewing sheet was readily produced, the adhesion to the substrate was good, and sharp recorded images were obtained, and as "X" where any one of the ink jet suitability, the glossiness of image viewing surface, the optical density of images, the adhesion and the sharpness of images was insufficient.

#### Example 6

A polyethylene terephthalate film used in Example 1 as a light-transmissive substrate was coated on its surface with the following Composition J by means of a bar coater so as to have a dried film thickness of 8  $\mu\text{m}$ , followed by drying in a drying stove at 120 °C for 5 minutes.

Composition J:	
Polyvinyl pyrrolidone (PVP K-90; produced by GAF; 10 % solution)	85 parts
Novolac phenol resin (Resitop PSK-2320; produced by Gun-ei Chemical Industry Co., Ltd.; 10 % DMF solution)	15 parts

Subsequently, the above coating was further coated with the following Composition K by means of a bar coater so as to have a dried film thickness of 20  $\mu\text{m}$ , followed by drying in a drying stove at 80 °C for 10

minutes.

Composition K:	
Ethylene/vinyl acetate copolymer resin (Flowback Q16079N; produced by Seitetsu Kagaku Co., Ltd.)	100 parts
Carboxymethylcellulose (Metollose 60SH; produced by Shin-etsu Chemical Co., Ltd.; 4 % aqueous solution)	25 parts
Polyoxyethylene octyl phenyl ether (Emulgen 810; produced by Kao Corporation)	0.3 part
Water	50 parts

The recording medium thus obtained was white and opaque. On this recording medium, ink jet recording was carried out in the same manner as in Example 1.

Thereafter, art paper (SA KinFuji Super Art; produced by Kanzaki Paper MFG. Co., Ltd.; basis weight: 157 g/m<sup>2</sup>) was superposed on the ink transporting layer, and then contact bonded thereto by using an iron (surface temperature: 130 °C) from the art paper side.

Evaluations of the resultant recording medium were also made following the procedures in Example 5. Results are shown in Table 3.

#### Example 7

A polyethylene terephthalate film used in Example 1 as a light-transmissive substrate was coated on its surface with the following Composition L by means of a bar coater so as to have a dried film thickness of 10 μm, followed by drying in a drying stove at 100 °C for 12 minutes.

Composition L:	
Polyvinyl pyrrolidone (PVP K-90; produced by GAF; 10 % DMF solution)	80 parts
Styrene/acrylic acid copolymer (Oxylac SH-2100; produced by Nippon Shokubai Kagaku Kogyo Co., Ltd.; 10 % DMF solution)	15 parts

Subsequently, the above coating was further coated with the following Composition M by means of a bar coater so as to have a dried film thickness of 20 μm, followed by drying in a drying stove at 70 °C for 10 minutes.

Composition M:	
Polyamide resin (Toin Thermotac SK-1; produced by Tokyo Ink Co., Ltd.; particle size: 20 μm)	100 parts
Styrene/butadiene rubber (ISR 6619; produced by Nippon Synthetic Rubber Co., Ltd.; solid content: 50 %)	15 parts
Polyoxyethylene (Emulgen A-500; produced by Kao Corporation)	0.2 part
Water	40 parts

The recording medium thus obtained was white and opaque. On this recording medium, ink jet recording was carried out in the same manner as in Example 1.

Thereafter, a glass plate (2 mm thick) was superposed on the ink transporting layer, and then contact bonded thereto by using an iron (surface temperature: 140 °C) from the substrate side.

Evaluations of the resultant recording medium were also made following the procedures in Example 5. Results are shown in Table 3.

Example 8

Composition L and Composition M used in Example 7 were coated on a tetrafluoroethylene film in the same manner as in Example 7, and thereafter the tetrafluoroethylene film was peeled off to obtain a white  
 5 opaque recording medium. On the recording medium, ink jet recording was applied in the same manner as in Example 1.

Thereafter, an aluminum foil was superposed on the ink transporting layer, and then contact bonded thereto by using an iron (surface temperature: 120 °C) from the aluminum foil side.

Evaluations of the recording medium were also made following the procedure in Example 5.

10 Results of the above are shown in Table 3.

Comparative Example 5

On the recording medium obtained in Comparative Example 4, recording was carried out in the same  
 15 manner as in Example 1. On the recorded matters obtained, art paper was superposed in the same manner as in Example 6, and then contact bonded thereto.

Evaluations on the resultant recording medium were made following the procedures in Example 5. Results are shown in Table 3.

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Table 3

	Ink absorbency (sec.)	Optical density of images	Image surface gloss (%)	Adhesion	Overall evaluation
Example 5	2	1.90	121.0	o	o
6	2	2.20	118.0	o	o
7	3	2.08	116.0	o	o
8	2	2.10	105.0	o	o
Comparative Example 5	1	1.72	116.0	x	x

55 Example 9

A polyethylene terephthalate film (100  $\mu\text{m}$  thick; produced by Toray Industries, Inc.) used as a light-transmissive substrate was coated on its surface with the following Composition N by means of a bar coater



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so as to have a dried film thickness of 10  $\mu\text{m}$ , followed by drying in a drying stove at 140°C for 10 minutes.

5	Composition N:	
	Cationic modified polyvinyl alcohol (PVA-C-318-2A; produced by Kuraray Co., Ltd.; 10 % aqueous solution)	100 parts
	Isocyanate compound (Elastron C-9; produced by Daiichi Kogyo Seiyaku Co., Ltd.; 10 % aqueous solution)	7 parts
10	Water-soluble melamine resin (Sumimarl M-50W; produced by Sumitomo Chemical Co., Ltd.; 10 % aqueous solution)	40 parts

Subsequently, the above coating was further coated with the following Composition O by means of a bar coater so as to have a dried film thickness of 20  $\mu\text{m}$ , followed by drying in a drying stove at 100°C for 5 minutes.

20	Composition O:	
	Polystyrene resin dispersion (L-8801; mean particle size: 0.5 $\mu\text{m}$ ; solid content: 45 %; produced by Asahi Chemical Industry Co., Ltd.)	100 parts
	Polyvinyl alcohol (PVA-117; 10 % aqueous solution; produced by Kuraray Co., Ltd.)	45 parts
25	Surfactant (Emulgen 810; produced by Kao Corporation)	0.2 part

On the recording medium, ink jet recording was carried out in the same manner as in Example 1, but by using the following four kinds of ink.

30	Yellow ink (makeup):	
	C.I. Direct Yellow 23	2 parts
	Diethylene glycol	15 parts
	Water	85 parts
35	Red ink (makeup)	
	C.I. Acid Red 92	2 parts
	Diethylene glycol	15 parts
	Water	85 parts
40	Blue ink (makeup)	
	C.I. Direct Blue 86	2 parts
	Diethylene glycol	15 parts
	Water	85 parts
45	Black ink (makeup)	
	C.I. Direct Black 19	2 parts
	Diethylene glycol	15 parts
50	Water	85 parts

The recording medium thus obtained was evaluated in the same manner as in Example 1. Results are shown in Table 4.

## Example 10

A polyester film used in Example 9 as a transparent substrate was coated with cationic modified polyvinyl alcohol (PVA-C-318AA; 10 % aqueous solution; produced by Kuraray Co., Ltd.) by means of a bar coater so as to have a dried film thickness of 5  $\mu\text{m}$ , followed by drying at 100°C for 10 minutes to form an ink retaining layer. Subsequently, the above coating was coated with a coating liquid having the following

makeup by means of a bar coater so as to have a dried film thickness of 45  $\mu\text{m}$ , followed by drying under the conditions of 140 °C for 5 minutes to form an ink transporting layer, whereupon a white opaque recording medium was obtained.

5	Coating liquid makeup:	
	Polymethacrylate resin (Microsphere M-100; mean particle size: 8 to 10 $\mu\text{m}$ ; produced by Matsumoto Yushi-Seiyaku Co., Ltd.)	100 parts
10	Polyvinyl alcohol (PVA-117; 10 % aqueous solution: produced by Kuraray Co., Ltd.)	100 parts
	Surfactant (Emulgen A-500; produced by Kao Corporation)	0.2 part
	Water	40 parts

15 Using the recording medium thus obtained, recording was carried out in the same manner as in Example 9 to make evaluations. Results are shown in Table 4.

#### Example 11

20 A polyester film used in Example 9 as a transparent substrate was coated with polyurethane ionomer (HYDRAN AP; produced by Dainippon Ink & Chemicals, Incorporated) by means of a bar coater so as to have a dried film thickness of 3  $\mu\text{m}$ , followed by drying at 100 °C for 10 minutes to form an ink retaining layer. Subsequently, the above coating was coated with a coating liquid having the following makeup by means of a bar coater so as to have a dried film thickness of 30  $\mu\text{m}$ , followed by drying under the conditions of 80 °C for 10 minutes to form an ink transporting layer, whereupon a white opaque recording medium was obtained.

	Coating liquid makeup:	
30	Low density polyethylene resin dispersion (Chemipearl M-200; solids content: 40 %, mean particle size: 5 $\mu\text{m}$ ; produced by Mitsui Petrochemical Industries, Ltd.)	100 parts
	Ethylene/vinyl acetate copolymer solution (Chemipearl V-100; solid content: 40 %; produced by Mitsui Petrochemical Industries, Ltd.)	10 parts
	Surfactant (pelex OT-P; active component: 70 %; produced by Kao Corporation)	0.2 part

35 Using the recording medium thus obtained, recording was carried out in the same manner as in Example 9 to make evaluations. Results are shown in Table 4.

#### Comparative Example 6

40 Commercially available OHP film (trade name: FP-AL10 Transparency; produced by Canon K.K.) was used to prepare a comparative recording medium.

Using this recording medium, recording was carried out in the same manner as in Example 9 to make evaluations. Results are shown in Table 4.

#### Comparative Example 7

45 Commercially available tracing paper (trade name: Tracing (mat); 40 g/m<sup>2</sup>; produced by Mitsubishi Paper Mills, Ltd.) was used to prepare a comparative recording medium.

50 Using this recording medium, recording was carried out in the same manner as in Example 9 to make evaluations. Results are shown in Table 4.

#### Comparative Example 8

55 Commercially available roll paper (trade name: Pure White Roll (HAMAYUU); 30 g/m<sup>2</sup>; produced by Kishu Paper Co., Ltd.) was used to prepare a comparative recording medium.

Using this recording medium, recording was carried out in the same manner as in Example 9 to make evaluations. Results are shown in Table 4.

## Comparative Example 9

Commercially available high quality paper (trade name: GINWA; 64 g/m<sup>2</sup>; produced by Sanyo-Kokusaku Pulp Co., Ltd.) was used to prepare a comparative recording medium.

Using this recording medium, recording was carried out in the same manner as in Example 9 to make evaluations. Results are shown in Table 4.

Table 4

## Example

(Evaluation items)	9	10	11
Ink fixing time	2 sec.	3 sec.	1 sec.
Image density			
Ink applying face (B)	0.60	0.72	0.57
Reverse face (A)	1.70	1.80	2.20
Glossiness	120.0 %	110.0 %	118.0 %
Overall evaluation	O	O	O

## Comparative Example

(Evaluation items)	6	7	8	9
Ink fixing time	5 min.	2 days	1 sec.	1 sec.
Image density				
Ink applying face (B)	1.20	1.30	1.26	0.95
Reverse face (A)	1.03	0.90	-	-
Glossiness	61.0 %	3.4 %	16.3 %	5.7 %
Overall evaluation	X	X	X	X

# Claims

1. A recording medium for use with an aqueous ink, said medium comprising an ink transporting layer and an ink retaining layer, the ink retaining layer having a greater absorption capacity than the ink transporting layer, the ink transporting layer being effective to receive and pass through the ink and having a high affinity for the liquid medium in the ink and a low affinity for colouring material in the ink wherein the ink transporting layer is light diffusive and wherein the ink retaining layer is light transmissive.
2. A medium as claimed in claim 1, wherein the ink transporting layer is porous.
3. A medium as claimed in claim 1 or 2, wherein the ink retaining layer is non-porous.
4. A medium as claimed in any preceding claim, wherein the ink transporting layer becomes adherent by the action of heat or pressure.
5. A medium according to any of claims 1 to 3, wherein the ink retaining layer is laminated on a light-transmissive substrate and the ink-transporting layer is further laminated thereon.
6. A medium according to any preceding claim, wherein the ink transporting layer comprises particles which do not become dyed by an intended recording agent, and a binder.
7. A medium according to any of claims 1 to 5, wherein the ink transporting layer comprises particles and a binder, the particles and the binder not having the property of fixing an intended recording agent.
8. The recording medium according to claim 6 or 7, wherein the weight ratio of the particles to the binder constituting the ink transporting layer is between 1/3 and 70/1.
9. A medium according to any preceding claim, wherein the ink retaining layer comprises a cationic resin and/or hydrophilic polymer.
10. A medium according to any preceding claim, wherein said ink transporting layer has intercommunicating holes.
11. A medium according to any of claims 1 to 9, wherein said ink transporting layer has internal fissures.
12. A medium according to any preceding claim, wherein said ink transporting layer has a thickness between 1  $\mu$ m and 300  $\mu$ m.
13. A medium according to any preceding claim, wherein said ink retaining layer has a thickness ranging between 1  $\mu$ m and 70  $\mu$ m.
14. A process for forming an image, comprising applying droplets of a recording liquid containing a dye, water and a water soluble organic solvent onto a recording medium as claimed in any preceding claim to form an image.
15. The process according to claim 14, wherein said recording liquid contains a dye at a concentration of 0.1 to 20 percent by weight.
16. A process according to claims 14 or 15, wherein the medium comprises a heat- and/or pressure adherent ink transporting layer and wherein after the ink droplets have been applied to the ink transporting layer the ink transporting layer is attached to a substrate.
17. A process according to claim 16, wherein the second substrate is paper, plastic, metal, glass or cloth.
18. A process according to claims 14 or 15, wherein the ink droplets are applied from the side of the ink transporting layer to form an image, and in which there is produced an image whose optical density (A) as measured from the side of the ink retaining layer is higher than the optical density (B) of the

image as measured from the side of the ink-transporting layer.

19. A process according to claim 18 wherein the ratio of optical density (A)/optical density (B) is 1.2 or more.

20. A process according to any of claims 11 to 19 carried out by ink jet recording.

21. A process according to any of claims 11 to 20 carried out by multi-colour recording.

# Patentansprüche

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1. Aufzeichnungsmaterial für die Anwendung mit einer wäßrigen Tinte, wobei das erwähnte Material eine Tintentransportschicht und eine Tintenfesthalteschicht umfaßt, wobei die Tintenfesthalteschicht ein größeres Aufnahmevermögen als die Tintentransportschicht hat, wobei die Tintentransportschicht derart wirkt, daß sie die Tinte aufnimmt und hindurchgehen läßt, und eine hohe Affinität für das flüssige Medium in der Tinte und eine niedrige Affinität für Farbstoffe in der Tinte hat, wobei die Tintentransportschicht lichtzerstreuend ist und wobei die Tintenfesthalteschicht lichtdurchlässig ist.

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2. Material nach Anspruch 1, bei dem die Tintentransportschicht porös ist.

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3. Material nach Anspruch 1 oder 2, bei dem die Tintenfesthalteschicht nicht porös ist.

4. Material nach einem der vorhergehenden Ansprüche, bei dem die Tintentransportschicht durch die Wirkung von Wärme oder Druck haftfähig wird.

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5. Material nach einem der Ansprüche 1 bis 3, bei dem die Tintenfesthalteschicht auf ein lichtdurchlässiges Substrat laminiert ist und die Tintentransportschicht ferner darauf laminiert ist.

6. Material nach einem der vorhergehenden Ansprüche, bei dem die Tintentransportschicht Teilchen, die durch ein gewünschtes Aufzeichnungsmittel nicht angefärbt werden, und ein Bindemittel umfaßt.

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7. Material nach einem der Ansprüche 1 bis 5, bei dem die Tintentransportschicht Teilchen und ein Bindemittel umfaßt, wobei die Teilchen und das Bindemittel nicht die Eigenschaft haben, ein gewünschtes Aufzeichnungsmittel zu binden bzw. zu fixieren.

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8. Material nach Anspruch 6 oder 7, bei dem das Masseverhältnis der Teilchen zu dem Bindemittel, die die Tintentransportschicht bilden, zwischen 1/3 und 70/1 liegt.

9. Material nach einem der vorhergehenden Ansprüche, bei dem die Tintenfesthalteschicht ein kationisches Harz und/oder ein hydrophiles Polymer umfaßt.

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10. Material nach einem der vorhergehenden Ansprüche, bei dem die Tintentransportschicht miteinander verbundene Löcher hat.

11. Material nach einem der Ansprüche 1 bis 9, bei dem die Tintentransportschicht Innenrisse hat.

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12. Material nach einem der vorhergehenden Ansprüche, bei dem die Tintentransportschicht eine Dicke zwischen 1 µm und 300 µm hat.

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13. Material nach einem der vorhergehenden Ansprüche, bei dem die Tintenfesthalteschicht eine Dicke zwischen 1 µm und 70 µm hat.

14. Verfahren zur Erzeugung eines Bildes, bei dem Tröpfchen einer Aufzeichnungsflüssigkeit, die einen Farbstoff, Wasser und ein wasserlösliches organisches Lösungsmittel enthält, auf ein Aufzeichnungsmaterial nach einem der vorhergehenden Ansprüche aufgebracht werden, um ein Bild zu erzeugen.

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15. Verfahren nach Anspruch 14, bei dem die erwähnte Aufzeichnungsflüssigkeit einen Farbstoff in einer Konzentration von 0,1 bis 20 Masseprozent enthält.

16. Verfahren nach Anspruch 14 oder 15, bei dem das Material eine durch die Wirkung von Wärme und/oder Druck haftfähige Tintentransportschicht enthält und bei dem die Tintentransportschicht an einem Substrat angebracht wird, nachdem die Tintentröpfchen auf die Tintentransportschicht aufgebracht worden sind.
17. Verfahren nach Anspruch 16, bei dem das zweite Substrat Papier, Kunststoff, Metall, Glas oder ein Gewebe ist.
18. Verfahren nach Anspruch 14 oder 15, bei dem die Tintentröpfchen von der Seite der Tintentransportschicht her aufgebracht werden, um ein Bild zu erzeugen, und bei dem ein Bild erzeugt wird, dessen von der Seite der Tintentfesthalteschicht gemessene optische Dichte (A) höher ist als die von der Seite der Tintentransportschicht gemessene optische Dichte (B) des Bildes.
19. Verfahren nach Anspruch 18, bei dem das Verhältnis optische Dichte (A)/optische Dichte (B) 1,2 oder mehr beträgt.
20. Verfahren nach einem der Ansprüche 11 bis 19, das mittels Tintenstrahlaufzeichnung durchgeführt wird.
21. Verfahren nach einem der Ansprüche 11 bis 20, das mittels Mehrfarbenaufzeichnung durchgeführt wird.

#### Revendications

1. Support d'enregistrement destiné à être utilisé avec une encre aqueuse, ledit support comprenant une couche de transport d'encre et une couche de rétention d'encre, la couche de rétention d'encre possédant une capacité d'absorption supérieure à celle de la couche de transport d'encre, la couche de transport d'encre étant apte à recevoir et laisser passer l'encre et possédant une forte affinité pour le milieu liquide présent dans l'encre et une faible affinité pour la matière colorante présente dans l'encre, la couche de transport d'encre ayant la propriété de diffusion de la lumière et la couche de rétention d'encre ayant la propriété de transmission de la lumière.
2. Support suivant la revendication 1, dans lequel la couche de transport d'encre est poreuse.
3. Support suivant la revendication 1 ou 2, dans lequel la couche de rétention d'encre est non poreuse.
4. Support suivant l'une quelconque des revendications précédentes, dans lequel la couche de transport d'encre devient adhérente sous l'action de la chaleur ou d'une pression.
5. Support suivant l'une quelconque des revendications 1 à 3, dans lequel la couche de rétention d'encre est stratifiée sur un substrat transmettant la lumière et la couche de transport d'encre est en outre stratifiée sur cette couche.
6. Support suivant l'une quelconque des revendications précédentes, dans lequel la couche de transport d'encre comprend des particules qui ne sont pas colorées par un agent d'enregistrement utilisé, et un liant.
7. Support suivant l'une quelconque des revendications 1 à 5, dans lequel la couche de transport d'encre comprend des particules et un liant, les particules et le liant n'ayant pas la propriété de fixer un agent d'enregistrement utilisé.
8. Support d'enregistrement suivant la revendication 6 ou 7, dans lequel le rapport pondéral des particules au liant constituant la couche de transport d'encre est compris dans l'intervalle de 1/3 à 70/1.
9. Support suivant l'une quelconque des revendications précédentes, dans lequel la couche de rétention d'encre comprend une résine cationique et/ou un polymère hydrophile.
10. Support suivant l'une quelconque des revendications précédentes, dans lequel la couche de transport d'encre possède des trous intercommunicants.

11. Support suivant l'une quelconque des revendications 1 à 9, dans lequel la couche de transport d'encre possède des fissures internes.
12. Support suivant l'une quelconque des revendications précédentes, dans lequel la couche de transport d'encre possède une épaisseur de 1  $\mu\text{m}$  à 300  $\mu\text{m}$ .
13. Support suivant l'une quelconque des revendications précédentes, dans lequel la couche de rétention d'encre possède une épaisseur de 1  $\mu\text{m}$  à 70  $\mu\text{m}$ .
14. Procédé de formation d'une image, comprenant l'application de gouttelettes d'un liquide d'enregistrement contenant un colorant, de l'eau et un solvant organique hydrosoluble à un support d'enregistrement suivant l'une quelconque des revendications précédentes pour la formation d'une image.
15. Procédé suivant la revendication 14, dans lequel le liquide d'enregistrement contient un colorant à une concentration de 0,1 à 20 % en poids.
16. Procédé suivant la revendication 14 ou 15, dans lequel le support comprend une couche de transport d'encre adhérent à chaud et/ou sous pression et dans lequel, après application des gouttelettes d'encre à la couche de transport d'encre, la couche de transport d'encre est fixée à un substrat.
17. Procédé suivant la revendication 16, dans lequel le second substrat consiste en un papier, une matière plastique, un métal, un verre ou une étoffe.
18. Procédé suivant la revendication 14 ou 15, dans lequel les gouttelettes d'encre sont appliquées du côté de la couche de transport d'encre pour former une image, et dans lequel est produite une image dont la densité optique (A), mesurée du côté de la couche de rétention d'encre, est supérieure à la densité optique (B) de l'image mesurée du côté de la couche de transport d'encre.
19. Procédé suivant la revendication 18, dans lequel le rapport densité optique (A)/densité optique (B) est égal ou supérieur à 1,2.
20. Procédé suivant l'une quelconque des revendications 11 à 19, mis en oeuvre par enregistrement par jet d'encre.
21. Procédé suivant l'une quelconque des revendications 11 à 20, mis en oeuvre par enregistrement en plusieurs couleurs.